# Laue X-ray backscattering of the high-temperature superconductor $HgBa_2CuO_{4+\delta}$

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An attempt is made to grow relatively large (>100 mg) single crystals of the cuprate superconductor $HgBa_2CuO_{4+\delta}$. A relatively large sample is seen in the boule of a growth and cut free using a wire saw. This sample is polished and is measured several times with Laue X-ray technique until an image is seen. Eventually, a coherent, four-fold symmetric pattern is seen, but the sample was polished too much and was destroyed in the process.

## Introduction

The phenomenon of superconductivity was first discovered by Dutch physicist Heike Kamerlingh Onnes in elemental mercury. This phenomenon manifests as a sudden drop to zero resistance in a material when cooled below a certain critical temperature ($T_c$), which depends on the material [1]. However, superconductivity exhibits another phenomenon, the Meissner-Oschenfeld effect, in which when cooled below its $T_c$, a superconducting sample expels all magnetic fields from its interior, causing it to maintain a net zero magnetic field within. A superconductor can therefore be described as a perfect diamagnet. While the infinite conductivity of a superconductor can be thought of as the idealized perfect conductor in classical physics, the Meissner-Oschenfeld effect cannot be explained classically, since exposing a perfect conductor to a constant magnetic field should result in a constant magnetic field within the material, according to classical predictions. Therefore, superconductivity must be a quantum mechanical phenomenon.

The theoretical description superconductivity was not established until 1957, when physicists Bardeen, Cooper, and Schrieffer first proposed the microscopic mechanism at work, which subsequently became known as BCS theory. This theory suggests that electrons interact with other electrons in the material through the pairing mechanism of phonons, which are simply the quanta of lattice vibrations in

the material [3]. Electrons are fermions, which obey the Pauli Exclusion Principle. As a result, they must occupy different energy states in order to avoid being in the same quantum state. However, in a superconductor, electrons form pairs with other electrons via phonons, forming what are called Cooper pairs, and the resultant pair has zero spin. Therefore, these Cooper pairs are effectively bosons, rather than fermions, which prefer to occupy the same energy state. Thus, when cooled below $T_c$, the Cooper pairs all occupy the same state of low energy, which is essentially responsible for conventional superconductivity.

BCS theory has been highly successful. However, in 1986, IBM researchers Georg Bednorz and K. Alex Müller discovered superconductivity in a ceramic material which had a critical temperature of 35 K [5]. This discovery was surprising for two reasons: the first being that the upper limit of critical temperatures predicted by BCS theory hovered around 30 K, and the second being that the material which this was discovered in was ceramic, while most superconductors up until then were elemental metals. Since then, more ceramic materials displaying superconductivity have been discovered, with critical temperatures being pushed higher and higher. These materials (along with other classes of materials with sufficiently high critical temperatures) have been aptly named high-temperature superconductors. These unconventional materials stood out even more when put under scrutiny of the isotope effect. For measurements of the isotope effect, atomic elements within a material are replaced with different isotopes of the same element. Since conventional superconductivity is due to lattice vibrations, it is expected that this swapping of the isotopes has a noticeable effect on the $T_c$. This is indeed seen for conventional superconductors. However, with the high-temperature superconductors, the observed isotope effect was orders of magnitude smaller than for conventional superconductors [8]. This effectively rules out phonons as the pairing mechanism of high-temperature superconductors. The search for the mechanism of high-temperature superconductors is one of the most sought-after answers in condensed matter physics today.

Of all the high-temperature superconductors, the most widely studied materials class are the cuprates, which are ceramic materials containing copper oxygen planes. These materials display a variety of interesting physical properties that depend on both the temperature of the material as well as its doping

level (i.e., the density of charge carriers). In order to see how the physical properties change with respect to these parameters, we can construct a schematic temperature vs doping diagram. This diagram is shown in Figure 1 below.

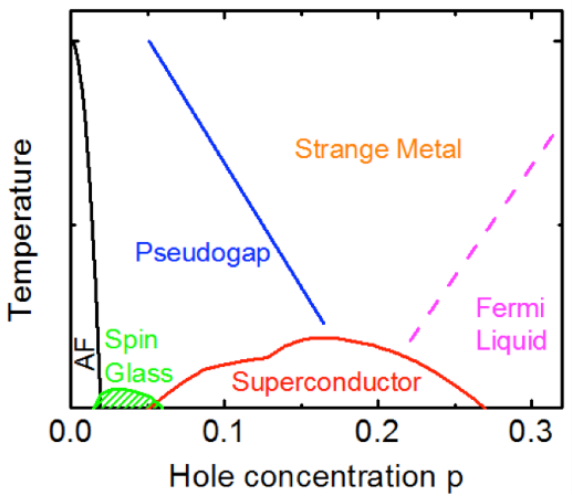


**Figure 1**: Generic temperature-doping phase diagram of the cuprates. The red line represents $T_C$.

This diagram has been constructed over years of experimentation and classification. Through these years, several additional phases of the cuprates have been discovered, which are not shown in the diagram. At zero doping, there exists a Mott-insulator phase that displays antiferromagnetic order. As charge carriers (holes) are added, the superconducting regime is eventually reached. It can be seen that the superconducting transition temperature ($T_c$) increases with doping until it reaches a maximum, and then decreases again back down to zero, forming a "superconducting dome." Other phases include the pseudogap phase at lower doping, which exhibits a partial energy gap on the Fermi surface of the material, the strange metal regime at intermediate doping, which displays T-linear resistivity, and the Fermi-liquid regime at sufficiently high doping, which exhibits conventional metallic behavior, including a quadratic temperature dependence of the resistivity. Due to the difficulty of producing and altering these materials, there are still regions of the phase diagram which have not been investigated to the fullest extent, but there is currently a large amount of effort exerted toward understanding the phase diagram as it

is. It should also be noted that due to the varying properties of these materials (e.g., disorder effects and crystal lattice structure), it is difficult to produce a generic phase diagram that applies to all cuprates. It is therefore highly desirable to study a material whose results can be generalized without worry of material dependence. This can be done with the model compound $HgBa_2CuO_{4+\delta}$ (Hg1201).

Hg1201 serves as an ideal compound for study for several reasons. It has a maximum $T_c$ of 98 K, which turns out to be the highest of all the single-layer cuprates [7]. Also, Hg1201 has a simple, tetragonal crystal structure. It is noteworthy that Hg1201 maintains this structure throughout accessible doping ranges, while other cuprates such as LSCO and YBCO undergo phase transitions which change their crystal structure [9]. This helps ensure that measured properties of Hg1201 does not depend on change in crystal structure. Rather, other more intrinsic properties must be at play. A third reason Hg1201 is a model compound is because disorder effects are relatively low compared to other cuprates. This is due to the relatively large distance of the disordered Hg-O layers from the quintessential Cu-O planes, where the superconductivity is believed to occur. Hg1201 was first discovered in polycrystalline form in 1993, but it is still desirable to obtain single crystals of this compound in order to verify its properties.

## Preparation and Crystal Growth

The growth process of Hg1201 involves the synthesis of mercury, oxygen gas, barium oxide, and copper (II) oxide. The balanced chemical equation is:

$$2Hg+O_2 + 4BaO+2CuO \rightarrow 2HgBa_2CuO_4$$

In our lab, relatively large, single crystals of Hg1201 are grown. The growth is a two-step process. First, $Ba(NO_3)_2$ and CuO powder are ground together with a mortar and pestle for a time totaling three hours. This resultant powder is then sintered at 900°C with oxygen inflow for 10 hours, to form the precursor $Ba_2CuO_3$. This step is necessary because the reactant BaO is unstable and reacts with $CO_2$ in the air. It also readily absorbs moisture. Carbon-based compounds can be very harmful to the growth, while moisture is known to enable the existence of impurities. Therefore, the precursor form of reactant is used.

Then, the precursor is ground up and 2.14 g is placed within a zirconia crucible. The crucible is then placed in a quartz tube, along with 1.5 g of HgO on the outside of the crucible. It was found before that placing the HgO on the outside of the crucible instead of inside the crucible resulted in less impurities [10]. The quartz tube is then sealed in a vacuum and placed in a high-temperature furnace, where the temperature program is set for the next 5 days. The program first ramps up to 800°C and stays there for 10 hours, which is where the reaction takes place. This reaction is dependent both on temperature and pressure, so sufficient Hg and $O_2$ partial pressure is needed. To ensure this, the quartz tube is sealed at a fixed distance from the bottom, which in this case is 10 cm. Once the reaction is finished, the temperature ramps up to 1020°C, which melts the compound and causes it to form a homogeneous mixture, or "flux." The program then cools to 900°C over the course of 60 hours, which when the single crystals form due to temperature gradients. This method of growing crystals is known as the flux method, and has proved to be very successful in growing single-crystals of Hg1201, as well as other compounds [6]. Once the program is finished, the quartz tube and crucible are broken open with a hammer and a resultant boule of flux is either placed in a humidity box to decompose or also broken open to look for crystals.

In addition to the required reactants, we also use some amount of hydrated magnesium sulfate ($MgSO_4$ x $H_2O$), which is placed within the quartz tube outside the crucible. It was once found that exposing the precursor to air for several minutes would result in larger crystals coming from the growth. It was concluded that this was due to the moisture in the air, which introduced impurities in the precursor and allowed sites for crystals to form. In order to make this process more controlled, the precursor is now exposed to air as little as possible and $MgSO_4$ is now used. The amount that is used depends on what size crystals are wanted; for neutron scattering, where sizable samples are desirable, 40-50 mg of $MgSO_4$ is used.

**Large Sample Preparation and Laue Scattering**

In order to make one neutron sample, many large single crystals of Hg1201 are needed. Sometimes, when a boule is broken open, the appearance of the side of a supposedly large crystal can be

seen. When this happens, the boule can be cut with a wire saw at the location of the grain boundary, separating the crystal from the rest of the boule. In order to ensure the crystal is single-grained, several iterations of polishing and Laue scattering must be performed.

The Laue X-ray backscattering technique of crystal diffraction is usually used to determine the orientation of a crystal sample [4]. However, this technique can also be used to determine whether a sample is a single crystal. The crystal structure of Hg1201 is known; it is tetragonal. This means that the ab-plane of the unit cell has four-fold symmetry, while any plane containing the c-axis has a two-fold symmetry. By the definition of the reciprocal lattice, this symmetry must also hold in reciprocal space. Therefore, when X-rays are incident on the ab-plane of a sample of Hg1201, we expect the backscattered pattern to have a four-fold symmetry. This is how we determine whether the sample is a single crystal or single-grained. If it is not, then either nothing is seen or many incoherent peaks are seen.

In order to perform these backscattering measurements, a Photonic Science Laue X-ray machine is used. The sample is fixed to a goniometer using wax, and is aligned with the X-ray beam. X-rays are then fired approximately normal to the sample, and are reflected backwards towards a screen, behind which CCD cameras measure the resulting pattern. If nothing is seen, the sample is removed and polished for several minutes, until it looks ready to measure again. This process is repeated until a pattern is seen or until the sample becomes too thin.

## Results

A potentially large sample (> 100 mg) was separated from the boule using the wire saw. This sample was then taken to the Characterization Facility at Shepard Labs, where the Laue machine was located. X-rays were incident on the ab plane of the sample. The sample went through several iterations of polishing, before an image was finally seen. This image is shown below in Figure 2.

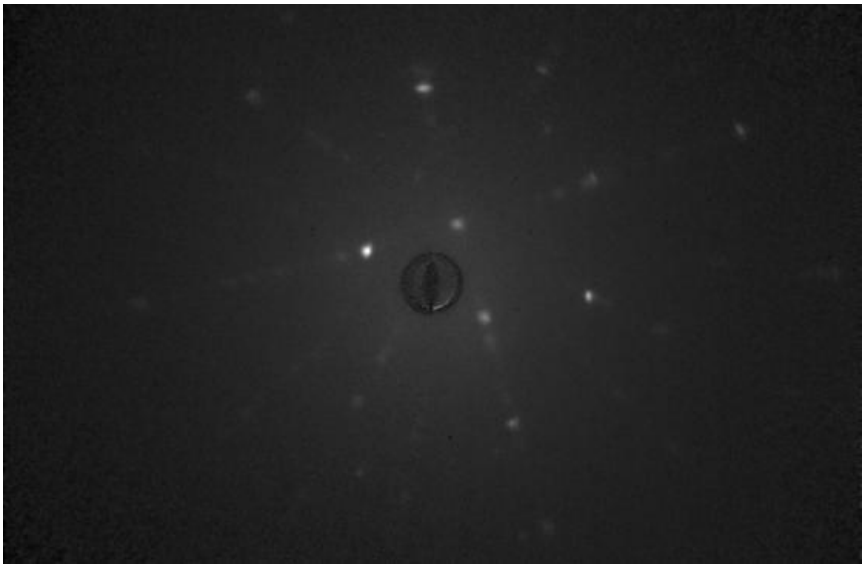

**Figure 2**: Four-fold symmetric pattern of a backscattered image of X-rays incident on the ab-plane of an Hg1201 sample. It can be seen that the pattern is rotated slightly, suggesting that the ab-plane of the sample is rotated as well.

Unfortunately, a better image could not be taken since the sample was subsequently destroyed from too much polishing. However, there is clearly a coherent pattern. This pattern has a nice four-fold symmetry, as was expected. The sample appears to have been oriented approximately 10° counterclockwise. The pattern is still a bit incoherent, suggesting that there may be very few misaligned grains adjacent to the main grain. Due to the symmetry of the pattern, it can be concluded that at least part of the sample was a single crystal. If the sample was not fractured as a result of the polishing, it would surely have been used as part of a neutron sample.

## Conclusion

Crystals of Hg1201 were successfully grown, and the Laue backscattered picture of a particularly large sample of Hg1201 was measured. Due to the coherent, four-fold symmetric pattern which was seen, it is likely that the sample was a single crystal.

Despite this conclusion, determining whether a potentially large sample is a single crystal is not the ultimate goal. It is imperative to obtain enough large samples to use in neutron scattering experiments.

Neutrons serve as an excellent probe of magnetic order and excitations in solids. Since neutrons have a magnetic moment, they can interact magnetically with condensed matter materials. They can also interact via the strong nuclear force with other nuclei. Since neutrons are neutral, and all the other interactions in question are short range, neutrons are able to penetrate far deeper in the material than ordinary particles, giving credence to neutron as a bulk probe [9]. To understand the influence of the potential interactions with the neutron, the transmission probability as a function of energy can be measured. In other words, understanding the input and the output can give information about scattering mechanisms. It is therefore highly desirable to continue to improve the crystal growth and to use this method of Laue backscattering (as well as other means) to ensure that large samples we have are single crystals of high quality, so that they can be co-mounted for a large sample to be used in cutting-edge neutron-scattering experiments.

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## References


[1] H. K. Onnes. *Comm. Leiden*, 122:2 (1911).

[2] W. Meissner and R. Ochsenfeld. *Naturwissenschaften*, 21:787 (1933).

[3] Bardeen et. al. Theory of Superconductivity. *Physical Review* **108** (5): 1175–1204 (1957)

[4] Ashcroft NW and Mermin ND. Solid State Physics. *Holt, Rinehart and Winston*, New York (1976).

[5] J.G. Bednorz and K.A. M¨uller. *Z. Phys. B*, 64:189 (1986).

[6] P.C. Canfield and Z. Fisk. Growth of single crystals from metallic fluxes. *Philosophical Magazine*, 65: 1117-1123 (1992)

[7] A. Yamamoto, W. Hu, and S. Tajima. *Phys. Rev. B*, 63:024504 (2000).

[8] Giustino et. al. Small phonon contriution to the photoemission kink in the copper superconductors. *Nature* **452**, 975-978 (2008)

[9] Yuan Li. Unconventional magnetic order and and excitations in the pseudogap phase of mercury barium copper oxide. *Thesis (Ph.D.) Stanford University* (2010)

[10] M. Veit. Transport measurements of the Cuprate Superconductor $HgBa_2CuO_{4+\delta}$. *Thesis (B.S.) University of Minnesota – TC* (2014).